Evaluation of Water Quality and Major Ion Concentrations in Background Waters in the Biere Aquifer Area

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Brief Summary of Pioneer Studies of the Regional Hydrogeochemistry

A preliminary investigation of the regional variation of the geochemical character of the non-impacted ground water of the Poplar River area aquifers suggest that the distribution pattern of dissolved constituents in these aquifers is not random and may be organized in a specific manner. Generally outside of the Poplar River flood plain the chemical character of the ground water changes progressively from east to west in the direction of the hydraulic gradient and these different hydrochemical facies appear to be defined within distinct geological settings related to the different glacial terraces and other geomorphological surfaces found in the area. These terraces (Terrace 1, Terrace 2, Terrace 3, the Ancestral Poplar River Valley, and the Modern Poplar River Valley) are described in the 2014 US Geological Survey (USGS) Scientific Report titled *"Delineation of Brine Contamination in and near the East Poplar Oil Field, Fort Peck Indian Reservation, Northeastern Montana, 2004–09"*. Figure 14 from this report (attached) show the general outlines of these terraces.

Regionally from east to west there appear to be three distinct types of water quality (facies) that can be recognized: 1) an area of relatively high mineral concentrations which carries water close to 5,000 mg/L total dissolved solids (TDS) which can be found along on the USGS Terraces 2 and 3 the older, upper bench glacial terraces; 2) a zone of moderately high ionic concentrations occupying the intermediate terrace designated as the Ancestral Poplar River Valley (heavy dashed black line on Figure 14). This area is defined geologically and geophysically by the USGS and Pioneer Natural Resources (Pioneer) as an area where the thickest basal gravels and sands occur along an older structurally low bedrock valley incised in the underlying Cretaceous Bearpaw Shale; and 3) a zone of relatively low ionic concentrations occupying the aquifer adjacent to the current path of the Poplar River.

The geospatial distribution patterns of dissolved constituents in the ground water between both the upper terraces and lower terraces and valley fill aquifers appear to be related to a few dominant factors. Elements that typically influence the dissolved major ionic composition in ground water are residence time (age of the water) as well as other important factors such as proximity to their recharge zones. For instance the uncontaminated ground water in the Poplar River flood plain and lower terraces are influenced by surface/ground water interactions and have some of the lowest ionic concentrations regionally. In the upper reaches of the Poplar River flood plain and lower terraces of the study area Pioneer has measured as much as 20 feet of change in water level in wells adjacent to the river. This water level change appears to be in direct response to surface water/ground water interactions and changes in the Poplar River discharge and fluctuations of river stage. Clearly ground water recharge in the Poplar River flood plain (USGS' Modern Poplar River Valley Terrace) and the Ancestral Poplar River Valley Terrace is mostly if not wholly from the Poplar River. Aquifers found on Terraces 1, 2 and 3 represent older former flood plains formed when streams flowed across these higher elevations areas. These abandoned higher terraces are not hydraulically connected to the Poplar River and therefore do not receive any recharge from the Poplar River. In addition to being topographically higher the aquifers on these terraces consists of the oldest glaciofluvial deposits in the area and therefore have waters of a much older age than waters located in the lower terraces found in the Modern and Ancestral Poplar River Valleys. The zone of recharge for the Biere #1-22 area is most likely from Slims Coulee approximately five mile to the northwest of the Biere #1-22 site. Water levels on the Biere upper terrace generally have a much smaller fluctuation on the order of from 4 to 6 feet although a few wells do exhibit a higher change in water level.

Pioneer Study of the Hydrogeochemistry of the PNR Mesa Biere #1-22 Area

Pioneer Natural Resources has conducted a "site-specific" study of uncontaminated background ground water in 14 wells situated in the Mesa Biere #1-22 plume area. All but three of the wells used in this study are identified in the 2014 USGS Scientific Report as being uncontaminated (represented as blue dots on Figure 14) and all wells are located on USGS Terrace 3 the same terrace as the Mesa Biere #1-22 plume (the upper Biere terrace). Two wells, the PNR40-12 and PNR41-12 wells included in the Pioneer study are not included in the 2014 USGS report because they were drilled after the limited five year (2004-2009) time frame for data used in the report. These wells while in very close proximity to the Biere Plume have ionic constituents consistent with the ranges of parameters defining uncontaminated water quality as published in the report therefore they are included in the set of uncontaminated wells. Monitor well MOC-5, not shown on Figure 14 of the USGS report was also added to the dataset. This well is located on Figure 5 of the USGS report and is also clearly located within Terrace 3 and exhibits ion concentrations similar to the other wells and is considered to be representative of uncontaminated background waters. In the Pioneer study the results presented in Table 1 represent the analyses of constituent values from all of the analytical sampling events during the period of record for each well rather than restricting the data to a five year period. Where available the Pioneer includes data through the latest sampling event through September 2014.

The Pioneer study shows that the hydrogeochemistry of the uncontaminated background waters on the USGS Terrace 3, the upper Biere Terrace appear to be variable in some of their major ion constituents. This variability in constituent values holds true not only geospatially across the terrace but appear to vary with time in any given individual well. Within the USGS Terrace 3 there are relatively high median concentrations of Total Dissolved Solids (TDS) and Sulfate (SO_4). All of the uncontaminated background ground water samples in the Biere #1-22 aquifer area exceed the USEPA secondary (aesthetic quality) maximum contaminant level (SMCL) for TDS and SO_4 in drinking water supplies of 500 mg/L and 250 mg/L respectively (USEPA, 2000). The average TDS value of all the non-impacted wells in the study is 4,250 mg/L. The average value for SO_4 in non-impacted waters on the Upper Bench Biere Aquifer is 2,111 mg/L. Although high in sulfate and TDS, all of the 14 wells in the study were below the SMCL for chlorides (Cl) with an average value of 98 mg/L. SO_4 is included in this study as it is a major ion that defines the hydrogeochemical facies of this area and sets it distinctively apart from the other areas. The SO_4 values in the water on this terrace will not change regardless of any ongoing brine removal operations and as such due to these high concentrations of SO_4 along with other constituents in the non-impacted water all of the water samples in the Biere Aquifer will forever also exceed the SMCL for drinking water for TDS at or above the average concentrations shown below in Table 1. The data used in this table is taken from the appendices table in the 2014 USGS Scientific Report and from the tables submitted semi-annually in Pioneer's reports to the USEPA.

Table 1, below, shows the maximum and minimum value of these constituents (Cl, SO_4 and TDS) in each of the 14 wells in addition to the average constituent value for each well. Note that the average constituent concentrations presented for each individual well in the table below is not the calculated average of the maximum and minimum values shown but rather the actual average tabulated for all of the analyses for each well. The number of analyses used to calculate the averages varies as each well has a different number of sampling events during the period of record. At the bottom of the chart, below the average constituent column is a number which represents the calculated average of the averages values listed above in the individual wells rows. Also shown at the bottom of the table is the range between the minimum and maximum values recorded for all wells in the table for each constituent. The maximum recorded constituent value in each well when compared to the corresponding minimum recorded value show that these constituent concentrations may vary from around 15% to as much as 70% within an individual wells sampling period or record. It is this variability within each wells sampling period of record that provides evidence for the potential misrepresentation of water quality when using a single data point in time as being representative of the water quality in and around the area of that particular well. In fact 50% (light brown shaded wells) of the background wells in the Biere #1-22 area have at one time or another had TDS values above the proposed 4,500 mg/L TDS level for cleanup. Basically, the average TDS values for these same wells are also at or above the 4,500 mg/L level.

Well Name	*Chloride Max*	*Chloride Min*	*Chloride – AVG*	*Sulfate - Max*	*Sulfate-Min*	*Sulfate-AVG*	*TDS-Max*	*TDS-Min*	*TDS-AVG*
MOC-5	190	103	147	3,170*		3,170	8,620		8,620
MOC-3	76	65	74	1,930	1,710	1,856	3,500	3,140	3,360
MOC-20A	388	112	156	3,390	2,760	3,199	5,500	4,800	5,274
PNR-16	33	9	22	3,460	2,360	3,020	5,110	3,430	4,852
PNR36-07	265	136	198	1,240	1,010	1,133	2,810	2,450	2,643
PNR-12	148	58	71	2,250	1,830	2,104	4,720	3,860	4,516
USGS92-12	15	3	6	1,840	733	1,235	3,160	1,610	2,186
MOC-1B	96	64	76	2,280	2,110	2,218	4,070	3,540	3,893
PNR-18	127	42	69	1,820	1,220	1,666	3,570	2,740	3,199
PNR33-06	134	73	106	2,700	2,390	2,570	4,890	4,170	4,476
PNR-29	181	81	106	2,150	1,860	2,015	4,960	4,250	4,723
LAW-MO1	26	17	22	1,430	1,120	1,285	2,910	2,350	2,628
PNR40-12	224	173	195	3,400*		3,400	7,660	6,670	7,200
PNR41-12	220	86	130	687*		687	1,990	1,830	1,935
AVERAGE VALUES	**152**	**73**		**2,226**	**1,737**		**4,534**	**3,449**	
AVG/AVG VALUE			**98**			**2,111**			**4,250**
Range of Values	**15-388**	**3-173**	**6-198**	**687-3,460**	**733-2,760**	**687-3,400**	**1,990-8,620**	**1,610-6,670**	**1,935-8,620**

Table 1. Maximum, Minimum and Average Values for Selected Uncontaminated Wells in the USGS Terrace 3-Biere #1-22 Area.

The most probable source of the elevated TDS and SO_4 in the waters all along Terrace 3 is the Late Cretaceous, Bearpaw Shale which crops out or is near the land surface throughout most of the Poplar River drainage area. In the Biere #1-22 area the gravels and sands are relatively thin and range from around 30 feet in the Biere #1-22 area (PNR-17) to just 10 feet or less in the western and lower reaches of the channel at the contaminant plume front (PNR-RW8). The Biere Channel itself is a glaciofluvial channel which is incised into and directly overlies the Bearpaw Shale. The Biere Channel is overlain by a thick section of very compact glacial till.

A detailed geochemical study of the Pierre Shale was conducted in 1962 by Harry A. Tourtelot with the United States Geological Survey (USGS). The Bearpaw Shale Formation is the geological equivalent of the Pierre Shale in North Dakota and other western and central states. His paper, titled *"Preliminary Investigation of the Geologic Setting and Chemical Composition of the Pierre Shale, Great Plains Region"* is an excellent reference for understanding the geological and geochemical nature of the Pierre Shale and its equivalent Bearpaw Shale. In this paper, a bed of weathered Pierre Shale (Bearpaw) in Fergus County, Montana was described. At this locality, joints and bedding planes in this roadcut were stained with iron oxides and coated with minute gypsum crystals. There were numerous iron and manganese concretions present as well. The iron oxides and sulfates, and gypsum were more abundant on the surface of the black shale than they were a foot or so beneath the surface. Core samples taken in this study also indicated that sulfide minerals, such as pyrite or marcasite, in the rock are oxidized to sulfate compounds at a very early stage in the weathering of an outcrop. No doubt the soils formed on this Cretaceous shale in this area are most likely rich in sulfate-bearing minerals (e.g., gypsum, pyrite, jarosite) all of which are the principal source of the high sulfate in the shallow ground water of the upper terraces in the Poplar River watershed. The USGS06-3 well on the western side of the Poplar River where there is only a very thin veneer of soils above the Bearpaw Shale has a SO_4 concentration >6,000 mg/L.

Picture 1 below shows a typical outcrop of Bearpaw Shale taken along the western margin of the Poplar River Valley. Shown in the picture are numerous beds of iron and manganese concretion nodules. This outcrop is very similar to the outcrop and core descriptions at other localities and is representative of the bedrock underlying the Biere #1-22 area and the USGS Terrace 3.

Picture 1-Outcrop of Bearpaw Shale on the western edge of the Poplar River flood plain showing typical weathering patterns of the Bearpaw Shale into low rounded hills. Seen in the outcrop are numerous thin beds of iron and manganese nodules.

Summary of Pioneer Evaluation of Water Quality and Major Ion Concentrations in Background Waters in the Biere Aquifer Area

Pioneer Natural Resources has conducted a "site-specific" study of uncontaminated background ground waters in 14 wells situated in the Mesa Biere #1-22 plume area. The purpose of the study was to determine reasonable "site-specific" water quality goals for their brine recovery and monitoring wells that are part of Pioneer's Biere #1-22 ongoing ground water remediation program and to determine when wells can be dropped from further recovery and monitoring activities as per site-specific closure criteria. Based on the extensive data set summarized in Table 1 for the Biere #1-22 Plume Area, Pioneer has proposed a SMCL cleanup level of either 250 mg/L chlorides or 4,500 mg/L TDS as a reasonable and technically sound targets for a well to be dropped from further monitoring and for site cleanup. Requiring remediation below these levels would mean that Pioneer would be cleaning up background concentrations.

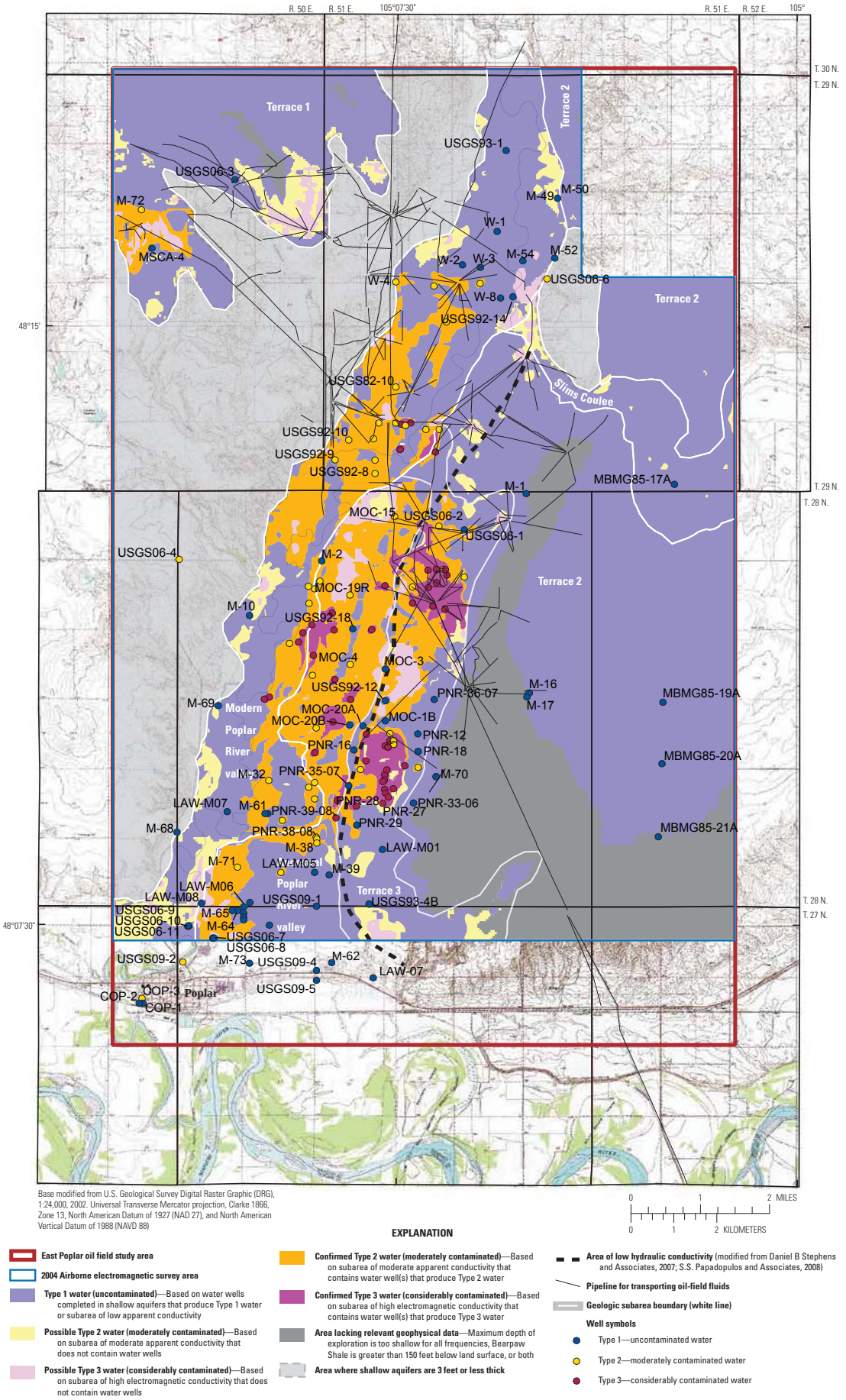

Figure 14. Delineating possible and confirmed areas of brine contamination in shallow aquifers, known pipelines, and types of water in shallow aquifers, in and near the East Poplar oil field study area, 2004–09.

Modified from Thamke, J.N, and Smith, B.D., Delineation of brine contamination in and near the East Poplar oil field, Fort Peck Indian Reservation, northeastern Montana, 2004-09; U.S. Geological Survey Scientific Investigations Report 2014-5024, pg. 31, http://dx.doi.org/10.3133/sir20145024.

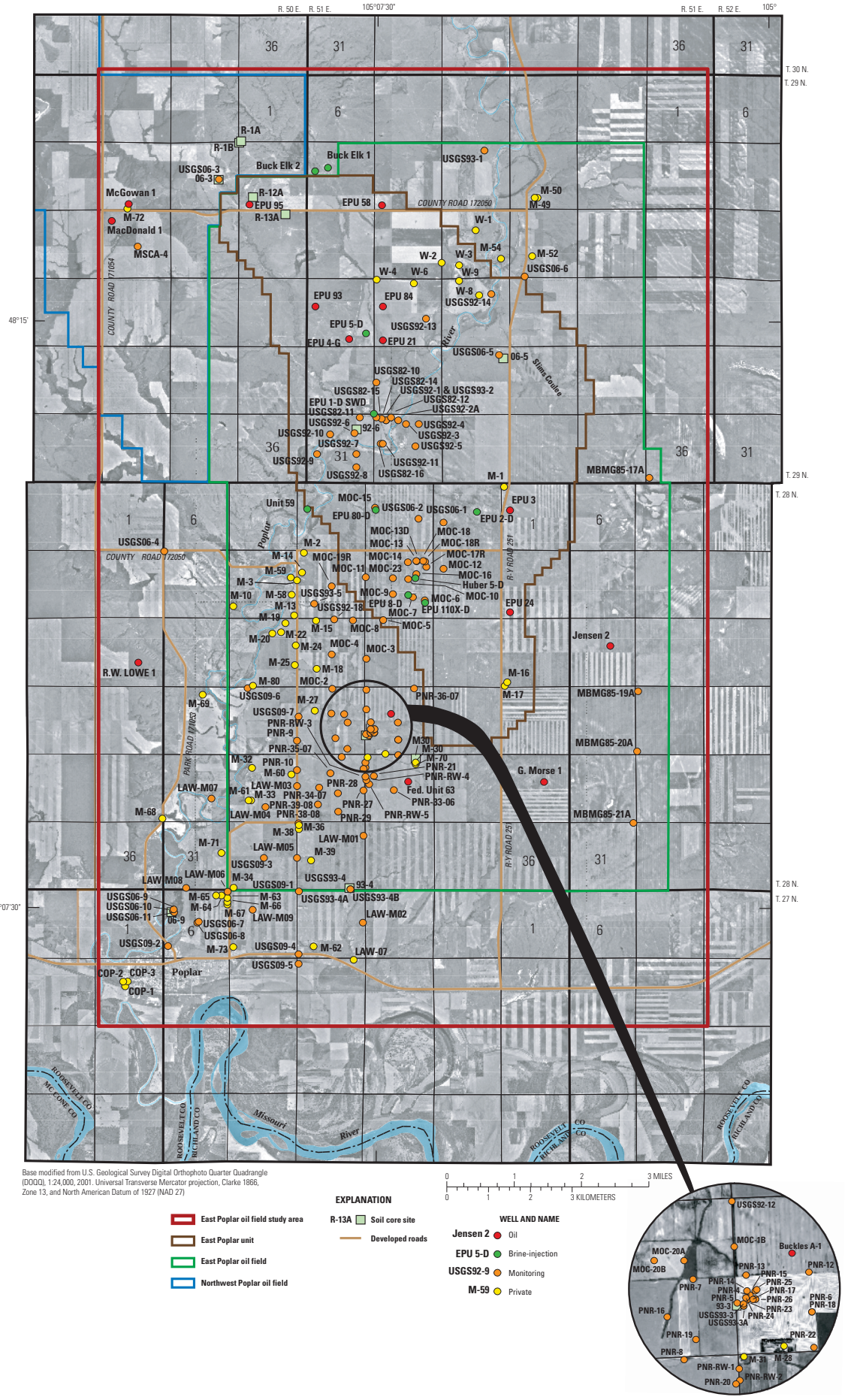

Figure 5. Locations of selected wells in and near the East Poplar oil field.

From Thamke, J.N, and Smith, B.D., Delineation of brine contamination in and near the East Poplar oil field, Fort Peck Indian Reservation, northeastern Montana, 2004-09; U.S. Geological Survey Scientific Investigations Report 2014-5024, pg. 10, http://dx.doi.org/10.3133/sir20145024.